

The present invention relates to a process for the upgrading of hydrocarbon mixtures that boil within the naphtha range and which contain sulfur impurities.

Specification Amendments

The specification has been amended at pages 9 and 13 to correct the spelling of heptamolibdate to heptamolybdate and to correct several formulas. None of the amendments introduce new matter into the case. Entry of the amendments is respectfully requested.

Claim Amendments

Claim 1 has been amended in order to place the format of the process claim in more conventional U.S. claim format. No substantive language changes have been made to the claim. Further, Claims 17 and 18 have been amended in order to place convert the language of these claims to the singular form. None of the amendments introduce new matter into the record nor raise new issues.

Newly added Claim 27 has been presented in order to more closely define the hydrocarbon mixture being treated by the present process in terms of a naphtha as described in the last paragraph on page 5 of the text. Entry of the claim into the record is respectfully requested.

Prior Art Rejection

As claimed, the present invention is a process of hydrodesulfurizing a hydrocarbon mixture, by reacting a hydrocarbon mixture containing olefins and having a boiling range

within the range of C₄ to 250° C, and a sulfur content of at least 150 ppm with hydrogen in the presence of a catalytic composition comprising:

a) an acidic carrier consisting of a silica and alumina gel, amorphous to X-rays, with a molar ratio SiO₂/Al₂O₃ of 30/1 to 500/1, having a surface area ranging from 500 to 1000 m²/g, a porosity of 0.3 to 0.6 ml/g and a pore diameter within the range of 10-40 Å;

b) a mixture of metals belonging to Groups VIB and VIII of the Periodic Table deposited on the carrier in an overall quantity ranging from 2 to 67 % by weight with respect to the total amount of components (a) + (b), thereby effecting said hydrosulfurization with concomitant skeletal isomerization of the olefins of said mixture.

Applicants place emphasis on the fact that the hydrocarbon mixture is one which boils within the stated range and is a mixture of both paraffinic hydrocarbons and olefins. In fact, a preferred embodiment of the hydrocarbon mixture is a full range naphtha having a boiling range of 35° -250° C. As a result of contacting the hydrocarbon mixture with hydrogen in the presence of the catalyst as defined in the claims, not only is significant hydrosulfurization of the mixture obtained, but also importantly from the viewpoint of obtaining a hydrocarbon product that exhibits a high octane rating, the olefin component of the hydrocarbon undergoes significant isomerization with minimal hydrogenation of the olefins to paraffinic material.

Claims 1-18 stand rejected based on 35 USC 103(a) as obvious over Hart U.S. Patent 3,156,640 in view of Bellussi et al EP-340868. This ground of rejection is respectfully traversed.

Although the Hart patent discloses a process of hydrogenating a hydrocarbon material that contains olefins over a metal containing supported catalyst that achieves

hydrodesulfurization, the hydrocarbon material of the patent is **not** that which is employed in the present process and further the metal containing catalyst is not that of the present invention.

As to the hydrocarbon material employed in the patent, the same is a combination of an olefin rich hydrocarbon mixture (see Example 1, col 5, lines 53-59) and a sulfur-containing hydrocarbon oil fraction that is said to have a low content of olefinic components (col 2, lines 40-42). (The sulfur containing hydrocarbon component functions as a diluent for the olefin containing paraffin in order to reduce the undesirable effects of excessive exothermicity of the hydroisomerization of the olefin component to isoparaffin materials.) The objective of the catalyzed hydrogenation reaction is not only reduction in the sulfur content of the product obtained, but also the isomerization of the olefins in the hydrocarbon mixture to isomeric structures while at the same time achieving reduction of the isomeric structures to saturated isoparaffins. (See column 1, lines 46-51. Note also as shown in Example 1 that extensive hydrogenation of olefins occurs as the olefin content (62 %) of the starting hydrocarbon mixture is reduced to the extent that the hydrocarbon product obtained is "practically free of olefins" (bromine number of < 1.) On the other hand, the hydrocarbon feed of the present process is not such a combination, but rather is a hydrocarbon mixture that boils within the stated range which contains from low to higher olefin contents. (A "full range naphtha" boiling over the range of 35° to 250° C is a particularly preferred hydrocarbon mixture employed in the process of the invention.) In the catalyzed reactions that occur, the olefins within the mixture are extensively isomerized to **unsaturated** isomers, however, with **minimal** reduction of the isomerized unsaturated isomers obtained to saturated isomers. The reason for the sought after minimal reduction of olefinic material is that the

presence of unsaturates in the hydrocarbon product yields a product of higher octane rating or number. Thus, the product desired and achieved by the present process which contains isomerized olefinic material that has experienced minimal reduction to saturated isomers is distinctly different from the reaction product of Hart that is "practically free from olefins."

The objective of the present process of olefin isomerization with minimal reduction during the hydrodesulfurization reactions which occur is shown, for instance, by the catalyst embodiment of the invention of Example 8 in Table 2 on page 20 of the text. Note that at the temperatures indicated, extensive hydrodesulfurization occurs as shown in the column "HDS%," significant amounts of isomerized unsaturated hydrocarbon remains as shown in the column "ISO%" relative to reduced hydrocarbon ("HYD%") and the ratio of HYD/ISO is 1 or slightly greater. On the other hand, for a comparative catalyst system as that of Catalyst F (Example 11), the columns ISO%, HYD% and HYD/ISO show a low content of isomerized unsaturates accompanied by extensive reduction of olefinic material to saturated hydrocarbons. Catalyst F, in fact, is a commercial catalyst of Co and Mo impregnated in a support of γ -alumina which is a type of catalyst within the scope of Hart.

A second important distinction of the invention as claimed over the Hart patent is that the present specific high silica content catalyst support is markedly different from the acid carriers described in column 4 of the patent which are stated broadly as silica, alumina and silica-alumina supports. There is absolutely no teaching or suggestion of the specific support of the present claims which has the specific characterizations set forth in Claim 1. Yet, it is the support of the catalyst system of the present process which enables the very desirable results obtained in the present invention for the production of a hydrocarbon product having a

relatively high unsaturated isomer content with minimal reduction of unsaturates to saturated hydrocarbon.

The deficiencies of Hart are believed to be neither overcome or improved upon by Bellussi et al. It is clear that the silica/alumina material disclosed in the reference is the same material which is used as the support for the catalytically active Group VIII and VIB metals used to prepare the catalyst system of the present invention which achieves the hydrodesulfurization results of the present invention. However, it must be noted that while the Examiner notes the disclosure in the publication that the catalyst system disclosed in the reference, which is the silica/alumina material described with no added metal, is useful in the catalysis of olefin isomerization reactions, nevertheless, the unsaturated feedstock is the like of the three types of olefinic materials taught in Example 10 of the publication which are 1-octene, a mixture of linear isomers of tetradecene and 7-tetradecene. The isomerization reaction does **not** occur in the presence of hydrogen. Moreover, whereas in the present process a significant degree of selectivity of olefin isomerization to isomeric unsaturated products is achieved while at the same time competing hydrogenation reactions that convert unsaturated material to isoparaffins and accomplish hydrogenative desulfurization of the feed to the reaction occur, no such competition occurs in the olefin isomerization reaction taught in Bellussi et al. Because the comparatively simple olefin isomerization process taught in the reference is fundamentally different from the hydrodesulfurization reaction of the present invention which occurs in the presence of a metal containing catalyst supported on the specific support described, one of skill in the art would not be led to attempt to preferentially use the silica/alumina isomerization catalyst taught by Bellussi et al as a support for a

catalytically active metal for use in a hydrodesulfurization reaction over any other silica, alumina or silica/alumina support known in the art.

Applicants stress with respect to the disclosure of Bellussi et al that the reactions catalyzed by silica-alumina gel in the reference are oligomerization, alkylation and isomerization reactions, for example, butene isomerization reactions. The isomerization reactions disclosed do **not** require hydrogen as a reactant, and accordingly, the isomerization reactions described are not conducted in the presence of hydrogen. Thus, with respect to isomerization, the only teaching in the reference is isomerization of olefins in the presence of the silica/alumina gel. There is no disclosure of the behavior of the catalyst when both hydrogen and olefins are present in the same reaction mixture. This is significant, because one of skill in the art would have expected that with the catalyst of the reference, when used in the presence of hydrogen, extensive hydrogenation of olefins would occur. To the contrary, it has now been surprisingly found that in the system as described in the present invention, where both olefins and hydrogen are present along with the acidic silica/alumina gel catalyst, it is possible to desulfurize the mixture of hydrocarbons containing sulfur and olefins while at the same time achieve skeletal isomerization of the olefins with a concomitant very low degree of hydrogenation of the of the double bonds of the olefin molecules.

In support of the comments immediately above, applicants refer to the data of the catalytic compositions of Hart, the data in Table 7 on page 24 of the present specification which show the superior (low) hydrogenation/isomerization (HYD/ISO) ratios of catalyst embodiments (B, C, E) of the present invention versus comparative catalysts F and G outside the scope of the invention, particularly catalyst G and the evidence in the table below of a

comparative catalyst similar to, but outside the scope of the present catalyst. (The data of the table will be formally presented into the record by way of a declaration.)

Temp (°C)	WHSV (hrs ⁻¹)	HDS (%)	ISO (%)	HDS/HYD	HYD/ISO
254	6.6	91.0	2.5	1.2	29.9
282	6.6	92.7	2.5	0.9	40.4

Accordingly, the combined prior art references do not suggest the invention as claimed and withdrawal of the rejection is respectfully requested.

It is now believed that the application is in proper condition for allowance. Early notice to this effect is earnestly solicited.

Respectfully submitted,

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IN THE SPECIFICATION

Please delete the paragraph bridging pages 9 and 10 in favor of the following new paragraph.

-- As far as the metal phase (b) of the catalyst is concerned, it can be introduced by means of aqueous or alcohol impregnation. According to the first technique, the silica and alumina gel, also in extruded form, is wetted with an aqueous solution of a compound of a metal of Group VIB, for example ammonium [heptamolibdate] heptamolybdate, the resulting product is dried, is optionally calcined, and is then impregnated with an aqueous solution of a compound of the metal of Group VIII, for example cobalt nitrate. It is then dried and calcined in an [oxidating] oxidizing atmosphere ranging from 200 to 600° C. Alternatively a single aqueous solution containing both compounds of the metals of Groups VIB and VIII can be used for contemporaneously introducing these metals. --

Please delete the paragraph of page 13, lines 4-20 in favor of the following new paragraph.

-- The gel thus obtained is bound with pseudoboehmite, the latter in a quantity of 39 % by weight with respect to the total weight of the calcined silica and alumina gel plus the ligand, extruded into cylindrical pellets and ground (40-70 mesh, $A_{sup} = 660 \text{ m}^2/\text{g}$). 10 g of the material thus obtained are then impregnated with 25 ml of aqueous solution containing 10.3 g of $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Ammonium [heptamolibdate])

heptamolybdate, hereafter called EMA) and left to rest at room temperature for 20 hours. The mixture is then dried in an oven in air at 110° C for 2 hours. The dried product is subsequently impregnated with 12 ml of aqueous solution containing 1.17 g of $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Cobalt nitrate, hereafter called CoN), the whole mixture being left to rest at room temperature for 20 hours. It is then dried in an oven in air at 110° C for 1.5 hours and calcined at 500° C for 4 hours, in air (rising rate: 180° C/hour). The chemical analysis of catalyst A relating to the metal content is indicated in Table 1. --

Please amend Claim 1, 17 and 18 as follows:

--1. (Amended) [The hydrodesulfuration of] A process of hydrodesulfurizing a hydrocarbon [mixtures] mixture, which comprises:

reacting said hydrocarbon mixture containing olefins and having a boiling [ranges] range within the range of C₄ to 250° C, [containing olefins] and a sulfur content of at least 150 ppm [of sulfur, with the contemporaneous skeleton isomerization of said olefins, which comprises putting these hydrocarbon mixtures in contact] with hydrogen in the presence of [with] a catalytic composition comprising:

a) an acidic [a] carrier [of an acid nature] consisting of a silica and alumina gel, amorphous to X-rays, with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 30/1 to 500/1, having a surface area ranging from 500 to 1000 m²/g, a porosity of 0.3 to 0.6 ml/g and a pore diameter within the range of 10-40 Å;

b) a mixture of metals belonging to Groups VIB and VIII of the Periodic Table deposited on the carrier in an overall quantity ranging from 2 to 67 % by weight with respect to the total amount of components (a) + (b), thereby effecting said hydrodesulfurization with concomitant skeletal isomerization of the olefins of said mixture.

17. (Amended) The process according to Claim 1, wherein the hydrocarbon [mixtures] mixture which [are] is subjected to hydrodesulfuration [are mixtures] is a mixture [having boiling ranges] that boils within the range of C₅ to 220° C.

18. (Amended) The process according to Claim 1, wherein the [catalysts are] catalyst is activated by sulfidation.--

Please add new Claim 27 as follows:

--27. (Newly Added) The process according to Claim 1, wherein the hydrocarbon mixture is a full range naphtha having a boiling range of 35° -250° C. --